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Global 3-D Modeling Studies Of Tropospheric Ozone And Related Gases

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1. Introduction

Our research was targeted at three issues: (1) the factors controlling ozone in the tropical troposphere, (2) the Asian outflow of ozone and its precursors, and (3) the causes of decadal trends observed in ozone and CO. We have also used support from this ACMAP grant to (1) work with Kelly Chance on the retrieval and interpretation of HCHO and NO_2 observations from GOME, and (2) develop GEOS-CHEM into a versatile model supporting the work of a large number of users including outside Harvard. ACMAP has provided the core support for GEOS-CHEM development. Applications of the GEOS-CHEM model with primary support from ACMAP are discussed below. A list of publications resulting from this grant is given at the end of the report.

2. General development and evaluation of the GEOS-CHEM model

The GEOS-CHEM model (http://www-as.harvard.edu/chemistry/trop/geos) is the latest generation of global 3-D models of atmospheric transport and chemistry at Harvard. It is driven by GEOS assimilated meteorological data from the NASA GMAO and builds on the original GEOS CTM developed by D. J. Allen. The horizontal resolution is $1°x1°$ in the GEOS-3 system (2000-) and $2°x2.5°$ in earlier versions. The GEOS-4 system replaced GEOS-3 in November 2002. It has $1°x1.25°$ horizontal resolution. The number of vertical levels ranges from 20 to 72 depending on the version (55 in GEOS-4). The boundary layer below 2 km is resolved with 6 or more vertical levels. Reanalysis of the 1991-2001 decade with GEOS-4 is being conducted at GMAO.

We have archived at Harvard the continuous GEOS data record from 1988 to present (except 1999) and have used these different data years for a large number of applications. In most cases the horizontal resolution was degraded to $2°x2.5°$ or $4°x5°$ for computational expediency. We have recently developed a one-way nested model capability to exploit the native resolution of the GEOS-3 and GEOS-4 data for regional simulations.

Bey et al. [JGR 2001] presented a first general description and evaluation of the GEOS-CHEM model for tropospheric ozone-NO_x-VOC chemistry. Results were contributed to the IPCC Ox-comp intercomparison of global tropospheric ozone models. Our general evaluation of model transport has included simulations of ^{222}Rn-^{210}Pb-^{7}Be to test continental convective transport, wet deposition, and stratosphere-troposphere exchange (STE) and of CH_3I (supported jointly by NSF) to test marine convective transport. Our aerosol ^{210}Pb-^{7}Be simulation introduced a new scheme for wet deposition including partial scavenging in wet convective updrafts, first-order rainout and washout from both convective anvils and large-scale precipitation, and cirrus precipitation. Simulation of ^{7}Be revealed excessive STE in the GEOS fields, which we correct

for now in the tropospheric ozone simulation by using the SYNOZ algorithm developed by M. Prather and colleagues.

A major new development in GEOS-CHEM has been the inclusion of coupled ozone-aerosol chemistry. In Martin et al. [JGR 2003], we applied off-line concentration fields for all major aerosol types from the GEOS-based GOCART model to examine radiative and chemical effects of aerosols not usually included in global ozone models. The Fast-J radiative transfer scheme used in GEOS-CHEM allows for Mie scattering by clouds and aerosols. We found that aerosols decrease surface $J(O(^1D))$ by 5-20% in most of the Northern Hemisphere. Uptake of HO_2 on aerosols accounts typically for more than 25% of total HO_x radical (HO_x = OH + peroxy) loss in continental boundary layers, and up to 50-80% over polluted regions of Eastern Europe and biomass burning areas in the tropics. Annual mean OH concentrations decrease by 9% globally and by 13% in the Northern Hemisphere as a result of these aerosol effects. Simulated CO concentrations increase by 5-15 ppbv, improving agreement with observations. Simulated O_3 concentrations in the boundary layer decrease by up to 15-45 ppbv over India during the biomass burning season in March, and by up to 5-10 ppbv over northern Europe in August, again improving comparison with observations.

Most recently we have developed a fully coupled aerosol-chemistry simulation by incorporating the GOCART aerosol modules into our tropospheric ozone-NO_x-VOC simulation, and adding simulations of NH_3 and of H_2SO_4-HNO_3-NH_3-H_2O thermodynamics.

3. Factors controlling tropical tropospheric ozone

A major focus of our ACMAP work has been the application of GEOS-CHEM to interpret tropical tropospheric ozone columns (TTOCs) retrieved from TOMS. In work reported by Martin et al. [JGR 2002a], we found that. GEOS-CHEM captures 44% of the variance of monthly mean TOMS TTOCs retrieved by the convective cloud differential method (CCD) with no global bias. There are major discrepancies over northern Africa and South Asia where none of the TOMS TTOC products reproduce the seasonal enhancements from biomass burning found both in the model and in MOZAIC aircraft data. A characteristic feature of these northern tropical ozone enhancements is that they are driven by the lower troposphere where the sensitivity of TOMS is poor due to Rayleigh scattering. We developed an efficiency correction using the LIDORT radiative transfer model that increases TOMS TTOCs over biomass burning regions by 3-5 DU and decreases them over oceanic regions by 2-5 DU, improving the agreement with in situ observations. The correction reduces by ~5 DU the magnitude of the "tropical Atlantic paradox" [Thompson et al., GRL 2000], i.e., the presence of a TTOC enhancement over the southern tropical Atlantic during the northern African biomass burning season in December-February. We reproduce the remainder of the paradox in the model and explain it by the combination of upper tropospheric ozone production from lightning NO_x, persistent subsidence over the southern tropical Atlantic as part of the Walker circulation, and cross-equatorial transport of upper tropospheric ozone from northern mid-latitudes in the African "westerly duct". These processes in the model can also account for the observed 13-17 DU persistent wave-1 pattern in TTOCs with a maximum over the tropical Atlantic and a minimum over the tropical Pacific in all seasons.

A remarkable feature of the TOMS TTOCs is the interannual variability in the tropics associated with ENSO. In a collaborative study with NASA/GSFC [Chandra et al., JGR 2002], we investigated the capability of GEOS-CHEM to reproduce this variability, focusing on the large El Nino in Sept.-Dec. 1997. The TOMS TTOC anomalies over the Pacific during this period show a broad enhancement over the western Pacific (extending well beyond the biomass burning region in Indonesia) and depletion east of the dateline. We reproduce this feature in

GEOS-CHEM and find that it reflects comparable contributions from biomass burning and from changes in convergence/subsidence patterns.

GEOS-CHEM features a pronounced summertime O_3 maximum over the Middle East, with mean mixing ratios in the middle and upper troposphere in excess of 80 ppbv. In Li et al. [GRL 2001] we showed that this model feature is consistent with the few MOZAIC aircraft observations in the region. It reflects large-scale subsidence of northern mid-latitude pollution transported in the westerly subtropical jet and of pollution and lightning outflow from South and East Asia transported in the easterly tropical jet. More observations in this region (in particular from satellite) are needed to confirm the presence of this O_3 maximum, which is of interest both as a test of our understanding of tropospheric O_3 chemistry and because of its implications for anthropogenic climate forcing.

4. Asian outflow of ozone and its precursors over the Pacific

There is considerable interest in better understanding the global atmospheric effects of ongoing Asian industrialization. The NASA/TRACE-P two-aircraft campaign conducted over the western Pacific in March-April 2001 addressed that issue by characterizing chemical outflow from different Asian pollution source regions (Jacob was mission scientist for TRACE-P). With ACMAP support we conducted two preparatory studies for TRACE-P, involving GEOS-CHEM analysis of observations from the NASA PEM-West B aircraft campaign [Bey et al., JGR 2001b] and from ozonesondes along the Pacific Rim [Liu et al., JGR 2002]. We report on these studies here.

In Bey et al. [JGR 2001b] we examined the sources and pathways for Asian outflow of ozone and its precursors to the Pacific in spring by simulation of observations from PEM-West B (Feb-Mar 1994). The highest pollutant concentrations over the western Pacific were in the boundary layer (0-2 km), both in the model and in the observations. However, the strongest outflow fluxes were in the lower free troposphere (2-5 km) due to lifting of pollution ahead of eastward-moving cold fronts. We found that this frontal lifting is the principal process responsible for export of both anthropogenic and biomass burning pollution from Asia in spring, and further found that fossil fuel combustion and biomass burning make comparable contributions to the budgets of CO, ozone, and NO_x in the Asian outflow. These results have since been confirmed by the TRACE-P observations. We found that anthropogenic emissions from Europe and biomass burning emissions from Africa make important contributions to the outflow north of 40°N (Europe) and in the upper troposphere at low latitudes (Africa), but the TRACE-P data indicate that these influences are difficult to differentiate from the background. Finally, we found that 13% of NO_x emitted in Asia is exported as NO_x or PAN, a smaller fraction than for the United States because of higher aerosol concentrations in Asia that promote heterogeneous conversion of NO_x to HNO_3. Nevertheless, springtime production and export of ozone from Asia in the model is much greater than from the United States in the same season because of stronger radiation.

In Liu et al. [JGR 2002], we examined the sources contributing to tropospheric ozone over the Pacific Rim in different seasons by applying GEOS-CHEM to the simulation of Hong Kong and Japanese ozonesonde observations for 1993-1997. Particular focus was placed on the extensive data set of 1996 observations from Hong Kong. We found that Asian pollution influence in the free troposphere is strongest in summer, while in the lower troposphere it is strongest in fall (low latitudes) and summer (mid-latitudes). The upper tropospheric ozone minimum and high variability observed over Hong Kong in winter reflects frequent tropical intrusions that recirculate Asian pollution brought southward into the ITCZ. Asian biomass burning makes a major contribution to ozone at <32°N in spring, not only in the lower free

troposphere but also in high-ozone layers brought to the upper troposphere by deep convection. We found maximum European pollution influence (<5 ppbv) in spring in the lower troposphere. North American pollution influence actually exceeds European influence in the model free troposphere, reflecting the pollution uplift by convection and by warm conveyor belts off the eastern seaboard of North America. Lightning influence on ozone over the Pacific Rim is minimum in summer because westward upper tropospheric transport at low latitudes carries the lightning outflow away from the Pacific Rim and towards the Middle East.

5. Retrieval and interpretation of HCHO and NO_2 data from GOME

We have collaborated with Kelly Chance (member of the GOME science team) on the retrieval and interpretation of HCHO and NO_2 columns from nadir solar backscatter measurements by GOME. GOME was launched in 1995 in a polar sun-synchronous orbit (local observation time is about 10:30 a,m.). Our work has focused on (1) developing an air mass factor (AMF) formulation to convert the fitted slant columns of HCHO [Chance et al., GRL 2000] and NO_2 into tropospheric vertical columns, (2) using the resulting vertical columns for top-down estimates of VOC and NO_x emissions.

The AMFs for HCHO and NO_2 depend on the vertical distribution of the gas because of strong atmospheric scattering in the UV. In Palmer et al. [JGR 2001], we introduced a new AMF formulation as the integral of the relative vertical distribution of the gas (shape factor) weighted by altitude-dependent coefficients (scattering weights) computed from the LIDORT radiative transfer model. The scattering weights are readily tabulated, and one can then obtain the AMF for any scene by using shape factors from a 3-D model simulation of that scene. This approach still allows independent evaluation of the 3-D model with the observed vertical columns, since the shape factor and the vertical column represent two independent pieces of information (although they may be correlated). Our scattering weights can be used by any 3-D model for their own comparisons to the GOME data. (Although it might seem preferable to compare slant rather than vertical columns to avoid model contamination, this only displaces the problem because the inverse of the AMF is needed to convert model vertical columns to slant columns. Vertical columns have the advantage of being geophysically meaningful.)

Application by Palmer et al. [JGR 2001] to GOME HCHO retrievals (340 nm) over North America in July 1996 using shape factors from GEOS-CHEM shows that the AMFs are typically 20-40% less over continents than over the oceans and are approximately half the values calculated in the absence of scattering. Because of the large GOME pixel size ($320x40$ km^2), scenes are rarely cloud free, but (in contrast to TOMS) GOME provides cloud fraction information for each scene. In this first study we simply excluded data with cloud fraction >40%, after verifying that lower cloud fractions did not induce apparent data bias (our more recent AMF calculation, applied to NO_2 as described below, resolves Mie scattering in the partly cloudy atmosphere). We found that the vertical HCHO columns in GEOS-CHEM capture respectively 50% and 60% of the variance in the monthly mean slant and vertical HCHO columns from GOME over North America in July 1996 (where the slant columns are uncontaminated by model data, and the vertical columns include AMF information from the model).

In more recent work [Palmer et al., JGR 2003], we developed a method for top-down mapping of reactive VOC emissions from the GOME HCHO columns. We showed that HCHO columns are linearly related to local VOC emissions, with a displacement length scale that increases with the VOC lifetime. We applied the method to GOME data for North America in July 1996, when isoprene is the main VOC responsible for the HCHO variance (and has a sufficiently short lifetime that the displacement length is negligible). Although terpenes also

represent a large fraction of biogenic VOC emissions, their HCHO yield is small. We conducted an indirect validation of the GOME HCHO columns by using GEOS-CHEM as an intermediary to compare GOME with in situ measurements of HCHO concentrations from surface and aircraft taken at different times. The GEOS-CHEM model, including the GEIA emission inventory for isoprene [Guenther et al., 1995], provides a good simulation of both the GOME HCHO columns (r^2=0.69, bias=+11%) and in situ surface measurements (r^2=0.47, bias=-3%), implying consistency between the two. The GOME observations show high values over regions of known high isoprene emissions (e.g., the Ozarks), and a day-to-day variability that is consistent with the temperature dependence of isoprene emission. Isoprene emissions derived from GOME over North America are 20% less on average than the GEIA values and almost twice the values from the U.S. EPA BEIS2 inventory. The bias due to filtering out cloudy scenes in the GOME data is estimated to be less than 10%. The GOME isoprene inventory when implemented in the GEOS-CHEM model provides a better simulation of the HCHO in situ measurements than either GEIA or BEIS2 (r^2=0.71, bias=-10%).

In Martin et al. [JGR 2002b] we presented a method for retrieval of tropospheric NO_2 columns from GOME that improves in several ways over previous retrievals including in the AMF calculation, the correction for a diffuser plate offset, and the quantification of errors. Stratospheric NO_2 columns were subtracted using latitude-dependent central Pacific data, and the resulting bias (due to non-zero tropospheric NO_2) was corrected using GEOS-CHEM and PEM-Tropics aircraft data. The AMF calculation improved on that of Palmer et al. by using local GOME information on cloud fraction, optical depths, and cloud tops to retrieve partly cloudy scenes using the Mie scattering capability of LIDORT. GOME is sensitive to NO_2 within clouds, in the same way that TOMS is sensitive to ozone within clouds. Over continental regions with high surface emissions, the AMF is typically 20-30% lower than clear-sky due to cloud obscuration.

Martin et al. [JGR 2002b] retrieved NO_2 columns globally for July 1996 and compared then with GEOS-CHEM values as a proxy for testing the underlying bottom-up NO_x emission inventory (GEIA for the anthropogenic component). Richter and Burrows [JGR 2002] attributed GOME NO_2 enhancements in the tropics to lightning, but we find that GOME should be relatively insensitive to lightning because of the low NO_2/NO_x ratio in the upper troposphere at 10:30 local time. Our retrieved NO_2 columns over the U.S., where NO_x emissions are relatively well known, are 18% higher than GEOS-CHEM and spatially correlated. Retrieved columns tend to be higher than GEOS-CHEM over industrial regions but are lower over Houston, India, eastern Asia, and the biomass burning region of central Africa.

6. Analysis of SHADOZ data (Southern Hemisphere Additional Ozonesondes).

We led an analysis of the QBO signals evident in the SHADOZ tropical sonde profiles [Logan et al., JGR 2003], and collaborated with A. Thompson on interpretation of the tropospheric data [Thompson et al., JGR 2003a,b]. We expanded our data base of monthly sonde statistics used for model evaluation (including GEOS-CHEM) [Logan, JGR 1999a,b] to include the SHADOZ profiles, and used these data in the study of tropical tropospheric ozone described above [Martin et al., JGR 2002].

SHADOZ provided the first in-situ equatorial ozone data, from Nairobi and San Cristobal (both 1°S), with a higher measurement frequency (weekly) than that of SAGE II in the tropics. The analysis of the QBO used sonde data from 1-18°S (SHADOZ) and 20°N (Hilo), as well as SAGE II data and the merged column ozone data set of R. Stolarski.

We identified some discrepancies between SHADOZ and SAGE II profiles in the equatorial stratosphere that appear to be caused by differences in procedures at various sonde stations. The

sonde data imply that ozone values above 50 hP are systematically higher over Nairobi than over San Cristobal, while SAGE data show no such difference. Co-located sonde/SAGE II profiles give the same vertical structure, but there are small offsets in absolute values above 50 hPa. Our QBO analysis uses monthly anomalies, so it is not affected by issues of absolute accuracy. However, differences in stratospheric ozone values of several percent are important in the context of using sonde data to critically evaluate SAGE II data.

The SHADOZ data reveal the dramatic change in shape of the equatorial ozone profile that accompanies the descent of the westerly shear zone. We found that the amplitude of the QBO anomaly, which extends from 15 to 80 hPa, exceeds ±20%, larger than indicated by earlier analyses of SAGE II data prior to 1991. Analyses of the QBO in column ozone have shown that there are periods when the sub-tropical signature is stronger in one hemisphere than the other, and sometimes missing in one hemisphere. There are two QBO signatures, or "cells" in the sub-tropical ozone profile, above and below ~20 hPa. We found that when there is a strong subtropical signature in column ozone, the two QBO cells in the ozone profile are of the same sign and reinforce each other; when the subtropical anomalies in column ozone are weak or missing, the upper and lower QBO cells in ozone are of opposite sign, and so cancel one another. Thus the QBO signals are not necessarily missing in the profile data. These differences are related to the timing of the equatorial winds with respect to the annual cycle.

7. Analysis of MOZAIC data.

We have used ozone profiles from the MOZAIC airborne program to supplement information on the spatial and seasonal distribution of ozone available from sondes. MOZAIC has provided some of the first regular ozone profiles from regions such as North Africa, the Middle East, and parts of south east Asia. These data were used to confirm the summer time ozone maximum found in the Middle East in tropospheric chemistry transport models [Li et al., GRL 2001] and to investigate the discrepancies between models and tropospheric ozone column measurements for northern Africa [Martin et al., JGR 2002]. In the latter study, the MOZAIC data show that ozone values are indeed highest in the northern biomass burning season, contrary to results derived from TOMS.

8. Model studies of trends in tropospheric ozone

We conducted a modeling study to examine the causes of regional differences in trends in tropospheric ozone [Fusco and Logan, JGR 2003]. Our analysis of the sonde data showed that ozone increased over Europe from the late 1960s until the middle 1980s, but has not increased since then [Logan et al., JGR 1999, and updated analysis to 2000]. Data for Japan show an increase in the 1970s, but little change since then. By contrast, there has been no trend in ozone over the United States, and a decrease over Canada up to 1993 [Logan et al., JGR 1999].

We used the GEOS-CHEM 3-D atmospheric chemistry and transport model, described by Bey et al. [JGR 2001], to explore various factors that might have contributed to the regional differences in tropospheric ozone trends [Fusco and Logan, JGR 2003]. Input of stratospheric ozone to the troposphere follows the SYNOZ method; a specified annual mean flux of ozone is input to the model in the tropical stratosphere, and the model transports stratospheric ozone as a separate tracer to the troposphere, where it undergoes photochemical removal. This method was adopted because previous work calculating the ozone flux from stratospheric concentrations led to cross-tropopause fluxes that exceeded observation-based estimates by factors of 3-4 [Bey et al., JGR 2001, Liu et al., JGR 2001].

Given the computation expense of many multi-year runs of the model, we explored the causes of the observed trends in tropospheric ozone with a series of sensitivity runs, using one year of model winds (1994). These included runs with fossil fuel emissions appropriate for 1970,

1985, and 1994, with the stratospheric flux changed by ±30%, with overhead column ozone for 1979-81 versus 1991-93 to examine the influence of changes in ultraviolet radiation, and with observed changes in tropospheric temperature. We found that we could account for some, but not all, features of the observed changes in tropospheric ozone if we allowed for the trend in precursors emissions and a 30% decrease in the flux of stratospheric ozone, due to decreases in ozone in the lowermost stratosphere. For example, the increase in emissions accounts for much of the increase over Japan and at least half of the increase over Europe since 1970 in spring and summer; the data show a much larger increase in fall and winter than the model. The model gives a small increase of ozone in the middle troposphere over Canada while the data show a decrease prior to the mid-1990s; however, allowing for a 30% decrease in the stratospheric flux gives a decrease in upper tropospheric ozone, particularly in winter and spring. Differences in meteorology could also have contributed to interannual variability and possibly to trends in tropospheric ozone. However, a recent simulation of the period 1979-1993 using ECMWF fields did not appear to capture observed interannual variability in mid-tropospheric ozone very well [Lelieveld and Dentener, 2000].

Analyses with the GEOS-CHEM model indicate that the stratospheric source of ozone contributes about 15-30 ppb of ozone to the region from 400 to 300 hPa in winter and 10-20 ppb in summer, for mid-latitudes; contributions below 700 hPa are <10 ppb in winter and <4 ppb in summer [Fusco and Logan, JGR 2002; Li et al., JGR 2002]. Other models find a much larger influence of the stratospheric flux on tropospheric ozone, but some of the differences may be caused by the method of assessing the stratospheric influence, and some by the use of a much higher input flux. There is also concern that deficiencies in cross-tropopause ozone transport may bias the results from GEOS-CHEM. The seasonal variation of ozone at 500 hPa is smaller in the model than observed, and the seasonal maximum occurs at least a month early at mid-latitudes. The model also underpredicts ozone somewhat in the upper troposphere, especially in spring [Bey et al., 2001; Li et al., 2002; Fusco and Logan, 2002], and underestimates the ozone gradient across the tropopause.

9. Biomass Burning Related Studies.

We have completed an assessment of biofuel use and burning of agricultural waste in the developing world, with partial funding from NSF [Yevich and Logan, GBC 2003]. This is the first such global analysis that allows for regional differences in the disposal of agricultural waste. Earlier estimates of biofuel consumption used United Nations FAO (Food and Agricultural Organization) statistics for firewood, which are thought to be low, and assumed that a uniform fraction of agricultural waste is burned everywhere [Seiler and Crutzen, 1980; Andreae, 1991; Hao and Liu, 1994]. For woodfuel consumption, we relied on energy assessments from the World Bank and other sources, based largely on survey data. Estimates of agricultural residue used as fuel were also taken from survey data where available. Otherwise we used information on the extent of the woodfuel deficit, together with patterns of residue use as fodder, construction material, mulch, and open field burning to estimate amounts used as household fuel.

We find that 1960 Tg dry matter was burned as biofuel in the developing world in 1985, of which 61% is fuelwood, 2% charcoal, 30% crop residues, and 7% dung; about 20% more was burned in 1995. In terms of carbon, this is 52% of the amount of fossil fuel burned in the same countries. Biofuel use generates emissions of 735 Tg CO_2 (C), 156 Tg CO, 10 Tg CH_4, and 2 Tg NO_x (N). About 400 Tg (dry matter) of crop residues are burned in the fields, giving rise to 140 Tg CO_2 (C), 23 Tg CO, 1 Tg CH_4, and 0.2 Tg NO_x (N). Our inventory is on a 1°x1° grid, and is available to the community. It is integrated into the GEOS-CHEM model.

We have developed methods to use satellite data to specify the time dependence of emissions from biomass burning [Duncan et al., JGR 2003]. The mean seasonal variation of biomass fires is derived from fire count data from the Along Track Scanning Radiometer (ATSR) and from the Advanced Very High Resolution Radiometer (AVHRR), while we use TOMS Aerosol Index (AI) data as a surrogate for the interannual variation in biomass burning in regions of the world where there is not an interfering signal from desert dust. We apply this surrogate to our mean inventory for emissions of CO, and find that there is no apparent trend in biomass burning emissions from 1979 to 2000, except that caused by the enhanced burning in 1997-98, attributed to the ENSO induced drought in Indonesia and elsewhere. There is considerable year-to-year variability, with a range of CO emissions from 400 to 565 Tg. Emissions are highest in 1997 and 1998 and lowest in 1979, 1984, and 2000. The time-dependent emissions inventory has been used in studies of aerosols [Chin et al., JAS 2002], pollution transport in and from Asia [Liu et al., JGR 2002; Staudt et al., JGR 2002a,b], and tropical ozone [Chandra et al., JGR 2002; Martin et al., JGR 2002] as well as in our own work on CO.

10. Model analysis of the budget, interannual variability, and trends in CO.

We have conducted a study of the budget, interannual variability, and trends of CO. We have simulated CO from 1988 to 1997 using the GEOS-CHEM model [Duncan et al. 2004, Duncan and Logan, 2004]. The model includes emissions from fossil fuel combustion, biomass fuel, and biomass burning that we have developed; it also includes CO produced by oxidation of CH_4, biogenic hydrocarbons (isoprene, monoterpenes, methanol, and acetone), and anthropogenic hydrocarbons. Emissions from fossil fuel vary yearly, based on published inventories for North America and Europe, and on UN data for liquid fuel use elsewhere [Bey et al., JGR 2001]; the emissions for biomass burning vary yearly, using the results described above. The concentration of OH is calculated with a parameterization scheme, allowing OH to respond to changes in CO, column ozone, H_2O, and other factors. We express the 24-h average OH as a set of high order polynomials in temperature, O_3 column, latitude, declination, concentrations of O_3, H_2O, NO_x, CO, CH_4, and other hydrocarbons [Duncan et al., JGR 2000]. The polynomials accurately represent OH as computed by the system of kinetic equations for the full chemical mechanism, with the computational cost reduced by a factor of 500. We have evaluated the model with measurements from NOAA/CMDL sites, as well as column CO data, and aircraft profiles. The model simulates correctly the seasonal cycle and amplitude of CO at many sites, as well as the interannual variability. The model simulates correctly the seasonal cycle and amplitude of CO at many sites, as well as the interannual variability. The mean bias between model and surface CO values is less than 10% at mid and high latitudes of both hemispheres, but the model underestimates tropical CO by 2-13%. The model reproduces the statistically significant decrease in CO found at high latitude sites, and at the long term record at Mauna Loa [Duncan and Logan, 2004]. The model reproduces the statistically significant decrease in CO found at high latitude sites [Duncan and Logan, 2004]. Our analysis shows that this is caused primarily by decreasing emissions of CO from Europe and the former Soviet Union, with a contribution from the decrease in the ozone column. We find that the burden of CO for 30°-90°N is influenced more by decreases in CO emitted in Europe and the former Soviet Union than by increases in CO from Asia because the former have a longer lifetime.

11. Publications supported by this grant.

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